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Copper dosing enhances nitrification in biofilters treating groundwater

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Nitrification in granular media filters is commonly used to remove ammonium (NH_4^+) during biological drinking water treatment. However, poor nitrification performance leads to excess ammonium in the finished water. This can result in unwanted nitrification in the distribution system, which can lead to loss of sufficient disinfectant residual (Zhang et al., 2009) and microbial aftergrowth (and thereby oxygen depletion, formation of toxic nitrite, corrosion, and taste and odor problems (van der Kooij, 2000)). In distribution systems without disinfection, residual ammonium is problematic because it prevents biologically stable water (Rittmann and Snoeyink, 1984).
Incomplete nitrification during treatment can be caused by lack of nutrients. Phosphorus for example has been shown to increase ammonium removal (Lytle et al., 2015). However, the nitrifying microorganisms also need other nutrients, such as trace metals, in comparably low amounts. Copper for example is vital for ammonia monooxygenase (Ensign et al., 1993), an essential enzyme which catalyzes the oxidation of ammonia to hydroxylamine, the first step in nitrification. Hence, we hypothesized that incomplete nitrification in biological filters could be caused by a deficiency of copper, and that dosing of the metal at low concentrations could help to overcome the limitations and stimulate the removal of ammonium.

Copper was dosed at ≤ 5 µg/L to the influent of a full-scale rapid sand filter at a groundwater treatment plant (GWTP) on Zealand, Denmark (Wagner et al., 2016 a). The plant had suffered from incomplete ammonium removal for several years. Treatment at the plant consists of simple aeration of the groundwater (through stairs aeration) and subsequent filtration with gravity driven rapid sand filters. Copper was dosed from solid copper rods, employing electrolysis (Albrechtsen et al., 2015; patent pending). Ammonium influent and effluent concentrations before and during dosing were monitored with an ammonium auto analyzer (Hach Lange, AMTAX™ sc). Furthermore, water was sampled over depth of the rapid sand filter and ammonium and nitrite concentrations were analyzed with colorimetric methods.

Copper dosing to the full-scale filter stimulated ammonium removal within only a few days (Fig. 1) and effluent concentrations dropped to <0.02 mg NH_4^+/L after only 20 days (Wagner et al., 2016 a). Correspondingly, volumetric ammonium removal rates [g NH_4^+/m^3 filter material/h] increased, thereby increasing the removal capacity.

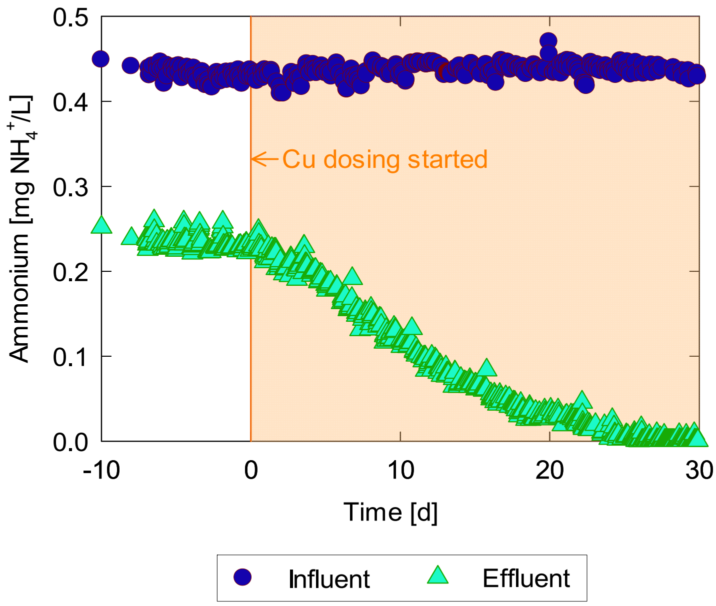

Figure 1 – Ammonium concentrations in the influent and effluent of a biological rapid sand filter at a full-scale groundwater treatment plant in Denmark. Copper dosing through electrolysis was started on day 0. (Adapted from Wagner et al., 2016 a)

Water sampling over filter depth revealed that ammonium removal activity was shifted upwards in the filter with onset of copper dosing. After 57 days with dosing, the volumetric ammonium removal rate for the top 10 cm of the filter had increased by a factor of almost 14 (Wagner et al., 2016 a). A second filter at the GWTP, which was monitored as a control and which did not receive dosing, did not show a change (neither positive nor negative) in ammonium removal performance.

Copper concentrations in the filter effluent were <1.5 µg Cu/L (Wagner et al., 2016 a) and therefore several orders of magnitude below regulatory limits such as the Lead and Copper Rule (USEPA, 2008) or EU (European Comission, 1998) and WHO (WHO, 2011) guidelines, and negligible compared with copper released from premise plumbing materials.

After our initial findings, we carried out a comprehensive investigation of 10 full-scale groundwater treatment plants (GWTPs) with nitrification problems and different treatment steps, filter design, water chemistry, etc. (Wagner et al., *submitted*). The study aimed at testing if copper dosing could generically stimulate ammonium removal, and at elucidating the effect on the microbial community in the filters. Before copper dosing, nitrification performance of the filters at the GWTPs was poor, and interestingly, regardless of different water chemistry at the sites, filter design, and ammonium loading rates, copper dosing at ~1 μg Cu/L stimulated nitrification in all 10 cases (Wagner et al., *submitted*).

Quantitative polymerase chain reaction (qPCR) and Illumina sequencing were used at 3 of the investigated sites to quantify and qualify the effect on the microorganisms in the filters. The analyses revealed that copper dosing did not only increase nitrification activity, but also the relative abundance of nitrifying microorganisms (Wagner et al., 2016 b).

The results from our studies let us conclude that controlled copper dosing can be a powerful tool to efficiently increase nitrification performance of granular media biofilters, stimulating nitrifier activity and abundance. The results have highly practical implications for water utilities operating biological filters. Increased nitrification capacity of biofilters is important and helps to make the filters more robust towards sudden shifts in ammonium loading rate, for example under dynamic operating conditions (Lee et al., 2014).

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